FIRST RESULTS FOR ETHYLPHOSPHINE, $CH_3CH_2PH_2$, FROM AN EFFECTIVE ROTATIONAL HAMILTONIAN FOR TWO-ROTOR SYSTEMS WITH SYMMETRIC AND ASYMMETRIC INTERNAL ROTORS (LIKE ETHANOL)

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Spectra of molecules with a 3-fold internal rotor become much more interesting in the presence of another large-amplitude motion (LAM) that leads to tunneling between equivalent asymmetric forms which may also tunnel to a different conformer. An effective rotational Hamiltonian has been derived for such a system of which ethanol, CH_3CH_2OH, is a typical example [a]. For isolated vibrational states of molecules with two symmetric rotors with sufficiently "high" barriers, the ERHAM code[b] works well. Modifications were explored to find out whether ERHAM can be coaxed to treat ethanol-type systems, using "ancient" unpublished microwave data from vibrational ground and excited states of ethylphospine, $CH_3CH_2PH_2$, as test data. For gauche ethylphosphine, the splitting between the a-type Coriolis-coupled ground states is 5.215(6) MHz whereas it is 229.9(2) MHz in the ν_{24} state (PH_2 torsion). The tunneling energy coefficients ϵ_{01} for the methyl internal rotation are -0.63(2) MHz and 2.93(5) MHz (sign undeterminable), respectively. These results look promising; however, up to now, sets of assigned frequencies had to be omitted from fits to experimental uncertainty of 25 kHz: (a) for the ground state, all c-type transitions $J_{4,J-3}$ - $J_{3,J-3}$ ($41 < J < 48$) for systematic large deviations (reason unknown); (b) for the ν_{24} state, half of the quartets of the $J_{3,J-2}$ - $J_{2,J-2}$ series ($28 < J < 32$) because of interactions with a state of the trans conformer) and some of the K_a = 1, 2 low-J transitions (incorrect assignments or unknown reasons). Analyses of data for the ν_{23} (CH_3 torsion) and ν_{22} (CCP deformation) states are in progress.

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[a] J.C. Pearson et al., J. Mol. Spectrosc. 251 (2008) 394

[b] P. Groner, J. Mol. Spectrosc. 278 (2012) 52–67